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NO DRAWINGS.

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COMPLETE SPECIFICATION.

Thermoplastic Elastomer Compositions.

We, THE INTERNATIONAL SYNTHETIC RUBBER COMPANY LIMITED, a Company organised under the laws of Great Britain, of Brunswick House, Brunswick Place, Southampton, Hampshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to cross linked polymers of butadiene and in particular to polymers of butadiene containing carboxyl groups which are cross linked by a thermally reversible process using metal ions.

Both rubbery and resinous plastic polymers show an increase in tensile strength if suitably cross linked. Normally, cross linking is carried out by means of sulphur vulcanisation or irradiation. Even simple polymers, such as polyethylene, show enhanced properties after irradiation. Cross linking is, however, usually an essentially irreversible reaction with the disadvantage that it must therefore be performed to the optimum level on any manufactured article during or after the moulding operation. This does not lend itself to quick repetitive operation and in the case of rubbers, laborious premixing of the vulcanisation ingredients prior to moulding and vulcanisation over periods of up to an hour at high temperature is necessary.

It has now been found that polymers can be synthesised containing functional groups which permit cross linking such that at normal working temperatures the material is tough and strong, but at higher temperatures, e.g. moulding temperatures, the cross links weaken to permit the polymer to be processed as a thermoplastic material. On cooling to ambient or working temperature the polymer once again attains its tough cross linked nature.

According to the present invention a thermally reversibly cross linked polymeric composition comprises a substantially linear homopolymer or copolymer of butadiene having attached thereto at least one carboxyl group per hundred polymerised butadiene units and as cross linking agent at least one hydrocarbon soluble alkoxide of a metal of groups 1—3 of the Periodic Table, cross linking of the carboxyl groups occurring via the metal ions.

Also according to the present invention we provide a method for preparing a thermally reversibly cross linked polymeric composition as just defined comprising treating the substantially linear homopolymer or copolymer of butadiene with a carboxylating agent as hereinafter defined and mixing the carboxylated polymer with at least one hydrocarbon soluble alkoxide of a metal from groups 1—3 of the Periodic Table.

The substantially linear homopolymer or copolymer of butadiene is preferably prepared by polymerisation of the appropriate monomers in a hydrocarbon solvent using an organo metallic catalyst. In this way the proportion of branching in the polymer is kept to a minimum. The stereo structure of the butadiene portion may be either low or high cis (e.g. 20—98% cis) depending on the particular catalyst system used in the preparation of the polymer. Both random and block copolymers, the latter containing two or more sequences, may be used in the present invention. The molecular weight of the polymer used should be in the range 5,000 to 3000,000 preferably in the range 50,000 to 150,000. Where a copolymer of butadiene is

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used the proportion of butadiene should desirably be greater than 50% by weight, e.g. 70%, suitable comonomers being for example, styrene, di-vinyl benzene and/or vinyl toluene.

The polymer need not be separated from the original polymerisation solvent(s) but may be used in solution in hydrocarbon solvent. Further hydrocarbon solvent may be added to the solution so that the concentration of polymer is e.g. from 5—15%.

The metal alkoxide may be chosen from the alkoxides of metals of groups 1 to 3 of the Periodic Table examples being sodium methoxide, sodium ethoxide, magnesium ethoxide and aluminium isopropoxide. The amount of alkoxide added may be up to 150% by weight based on the carboxyl content of the polymer preferably from 70—120%.

In order to obtain optimum results the addition of diols or polyols e.g. glycerol as well as conventional plasticisers e.g. dibutylphthalate or mineral oils or waxes is desirable to improve the flow properties of the final polymeric composition.

Metal oxides especially mono, di or tri basic oxides or mixtures thereof may be included as reinforcing agent enabling a higher tensile strength to be obtained. Predominantly di basic metal oxides e.g. magnesium and zinc oxides are preferred but other oxides, for example oxides of potassium, calcium, barium, cadmium, and aluminium may be included. As well as metal oxides, other conventional reinforcing agents such as carbon black may be included in the composition.

To obtain the thermally reversibly cross-linked polymeric composition it is preferred that the substantially linear homopolymer or copolymer of butadiene having carboxyl groups attached thereto is treated in organic solvent solution with the hydrocarbon soluble alkoxide(s) and cross linking is thereby achieved by removal of the corresponding alcohol (e.g. methanol where a methoxide has been used). Cross-linking via this method gives very good clear products which have excellent tensile strength and good elongation at break as well as good flow properties.

The substantially linear homopolymer or copolymer of butadiene having attached thereto at least one carboxyl group per hundred polymerised butadiene units may be obtained by treating a substantially linear polymer of butadiene with a carboxylating agent. A carboxylating agent is defined herein as meaning any agent containing carboxylic groups which will react with a polymer of butadiene so that carboxyl groups become attached to the polymer chain at the carbon atoms of the carbon-carbon double bonds. Preferably the carboxylating agent is a thiol carboxylic acid e.g. mercapto acetic acid (thioglycollic acid), α and β mercaptopropionic acid and mercaptosuccinic acid. Thioglycollic acid is very suitable. Conventional free radical initiators may be used to catalyse the carboxylation reaction e.g. peroxides, hydroperoxide and azo compounds.

A convenient method of carboxylating the polymer in this way is to add a suspension of 2,2^1 azo bis isobutyronitrile in thioglycollic acid to the hydrocarbon solution of the butadiene polymer and to subject the mixture to viborous agitation, followed by heating to 60°C. At this temperature the reaction proceeds.

The concentration of 2,2^1 azo bis isobutyronitrile used is usually between 0.25 to 0.5% by weight based on the weight of the polymer. The amount of thioglycollic acid or other carboxylating agent is preferably such that from 1 to 15% of the double bonds of the butadiene are carboxylated although higher degrees of carboxylation are not excluded.

To recover the carboxylated polymer from the hydrocarbon solution a second solvent in which the polymer is insoluble may be added. Alternatively the polymer solution may be pumped into e.g. an equal volume of an aqueous soap solution containing approximately 1 part of soap per hundred parts of rubber and the mixture agitated so that an emulsion is formed. This emulsion is then pumped into a steam heated vessel held at a temperature of 100°C. and the solvent and carboxylating agent removed by steam distillation.

When prepared in this way it is important that an anti gelling agent should be included with the carboxylated polymer since, on processing, carboxylated elastomers tend to decompose by scission of the C—S bonds to free radicals. Further reaction of these free radicals leads to non-reversibly cross-linked polymers which have an adverse effect on the processability of the reversible cross linked polymers. The anti gelling agent may have various chemical compositions but those which have a marked affinity for free radicals are useful, e.g. thiol compounds, mercaptonaphthyl compounds, organic disulphides and long chain alkylated phenols and trialkyl aryl phosphites for example a mixture of tris nonyl phenyl phosphites known as POLYGARD (registered trade mark). Polygard is very suitable since it also acts as a lubricating plasticiser.

The following examples illustrate the invention.

EXAMPLE 1

A polybutadiene having a molecular weight of 80,000 as determined by Intrinsic viscosity measurement was treated so that 2.75% by weight of the carbon-carbon double bonds were modified by attachment of carboxyl

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